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AIR RESOURCES BOARD

**Ambient Air Monitoring for Oxydemeton-methyl in Monterey County
During August and September 1995**

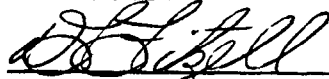
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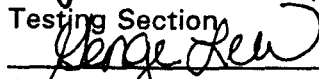
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Ambient Air Monitoring for Oxydemeton-methyl in Monterey County
During August and September 1995

This report presents the results of ambient air monitoring in Monterey County for oxydemeton-methyl (Metasystox R, MSR) and its primary breakdown product, dioxydemeton-methyl during the peak use period of August and September. Samplers were set up in various towns near expected application sites. The limit of quantitation for oxydemeton-methyl and its breakdown product was 0.25 ug/sample (0.012 ug/m³ for a 24-hour sample collected at 14.6 lpm). A total of 90 samples (including duplicates and 4 blanks) were collected and analyzed for both compounds. No oxydemeton-methyl nor dioxydemeton-methyl was found above the limit of quantitation. Three samples had trace levels (0.05 to 0.25 ug/sample) of one or the other compound.

Acknowledgments

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I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board's (ARB) Air Quality Measures Branch, the ARB Engineering and Laboratory Branch (ELB) conducted a four-week ambient monitoring program for oxydemeton-methyl (Metasystox R, MSR) and its primary breakdown product, dioxydemeton-methyl, in Monterey County during the summer of 1995. This monitoring occurred from August 14 through September 8, 1995. The peak use of oxydemeton-methyl is during the summer as an insecticide on cauliflower and broccoli. As required by the Food and Agricultural Code 14021, this monitoring was conducted to provide the DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

As part of the requirement of DPR, the ARB was also monitoring an application of oxydemeton-methyl in Monterey County around the same time as the ambient monitoring program. The results of the application monitoring are presented in the ARB report, "Ambient Air Monitoring After an Application of Oxydemeton-methyl in Monterey County During September 1995."

The Pesticide Use Report for 1994 indicates oxydemeton-methyl is most widely used on broccoli (52,282 pounds), cauliflower (23,627 pounds), sugar beets (9,288 pounds), and cabbage (8,729 pounds).

This monitoring was a follow-up to similar sampling conducted in September 1992 which found no measurable levels of oxydemeton-methyl or dioxydemeton-methyl in either ambient or application monitoring. The present monitoring was undertaken because it was felt the limits of quantitation for 24-hour samples (6.0 ug/m^3 for oxydemeton-methyl and 4.5 ug/m^3 for dioxydemeton-methyl) in the previous study were not low enough to evaluate the potential health risks.

II. DESCRIPTION

Oxydemeton-methyl (molecular weight 246.29 g/mole) is a colorless liquid with a vapor pressure of 3.83×10^{-5} mm Hg at 25°C. It is only slightly soluble in water (approx. 1.0×10^{-5} ppm), but is readily soluble in dichloromethane, 2-propanol and toluene.

Oxydemeton-methyl is regulated as a restricted use material under Section 6400, Title 3 of the California Code of Regulations and classified a Category I pesticide by the United States Environmental Protection Agency (US EPA). Peak use of this insecticide occurs in Monterey County during late summer (July, August and September).

The acute oral and dermal LD_{50} (rat) for oxydemeton-methyl is 60 mg/kg and 112 mg/kg,

respectively. Female rat and mouse LC_{50} values are 1.5 and 0.51 mg/L, respectively. (DPR's Monitoring Recommendation, APPENDIX I.)

III. SAMPLING LOCATIONS

The 1993 Pesticide Use Report (PUR) indicated that the highest usage of oxydemeton-methyl occurred in Monterey County during the summer months. This information along with the recommendations of the Monterey County Agricultural Commissioner's Office was used to determine which locations would be expected to be near oxydemeton-methyl applications. As a result, five sites were selected: one in northern Salinas at the La Joya School (site LJ), one in Chualar (site C), one near Soledad (site S), one in Greenfield (site G) and one in Prunedale (site P) which was the urban background site. Three samplers were on roof tops (approximately 15 feet above ground): site P, site LJ and site C. The two remaining sites (site S and site G) were on ground level (approximately 1.5 meters above ground). TABLE I lists the addresses or locations of the monitoring sites. FIGURE I shows the location of these monitoring sites. In addition, a second sampler was rotated among the sites to obtain duplicate collocated samples which were designed to evaluate the precision of the data.

The sites were chosen on the basis of the criteria listed in the Quality Assurance Plan for Pesticide Monitoring (APPENDIX II, Attachment II). Other considerations in selecting the monitoring sites were: proximity to expected application sites, possible population exposure, reasonable access, availability of AC power, and security.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through a Teflon holder containing approximately 30 cc of XAD-4 resin (see APPENDIX II). The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any oxydemeton-methyl or its breakdown product present in the sampled ambient air was captured by the XAD-4 adsorbent. Subsequent to sampling, the resin was transferred into a glass jar with a Teflon-lined lid and stored in an ice chest containing dry ice. All samples were transported on dry ice to the Trace Analytical Laboratory (TAL) of the Department of Environmental Toxicology, University of California, Davis for analysis.

Each sample train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, rotometer, train support, and a 12VDC powered vacuum pump. A diagram of the sampling train is shown in APPENDIX II, Attachment I. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through the holders adjusted with a metering valve to an indicated reading of 15.0 liters per minute (lpm) on the rotometer. A leak check was performed by blocking off the sample inlet. The sampling train would be considered to be leak free if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 15.0 lpm. The starting flowrate (if different

from the 15.0 lpm) along with date, time and site location were recorded in the field log book. Calibration prior to use in the field indicated that an average flow rate of 14.6 lpm was actually achieved when the flow meter was set to 15.0. At the end of each sampling period the final indicated flow rate (if different than the set 15.0), the stop date and time were recorded. If the final flow rate changed from the original set value, the average of the initial and the final flow rates was used to calculate the total volume of sampled air.

V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the TAL staff. The XAD-4 resin was extracted with 75 ml ethyl acetate. An aliquot of the extract was evaporated to dryness then redissolved in acetone prior to analysis using gas chromatography/nitrogen-phosphorus detector (GC/NPD). This analysis was to determine levels of the breakdown product, dioxydemeton-methyl, present in the sample.

To obtain the parent compound concentration, a second aliquot of the sample was oxidized and analyzed for combined dioxydemeton-methyl (any originally in the sample plus any oxydemeton-methyl present which would be oxidized to the breakdown product, dioxydemeton-methyl) using GC/NPD. The level of oxydemeton-methyl was calculated by subtracting the non-oxidized results from the oxidized results from the same sample. A detailed description of the method is presented in the TAL Report (APPENDIX III).

VI. RESULTS

Results for oxydemeton-methyl are shown in TABLE II and APPENDIX III. The QA/QC data are presented in APPENDICES II and III. The reported volumes (TABLE II) were calculated using the average of the beginning and ending flow rates.

The limit of quantitation for oxydemeton-methyl and its breakdown product was 0.25 ug/sample (0.012 ug/m³ for a 24-hour sample collected at 14.6 lpm) for each. A total of 90 samples (including duplicates and 4 blanks) were collected and analyzed for both compounds. No oxydemeton-methyl nor dioxydemeton-methyl was found above the limit of quantitation. Three samples had trace levels (0.05 to 0.25 ug/sample) of one or the other compound. In this report, if the TAL was unable to quantify the level, it is reported as not detected (ND). The TAL Report (APPENDIX III) identifies the samples which contained trace levels. Fifteen samples were collected at each site, excluding duplicate samples.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the TAL Report for oxydemeton-methyl and dioxydemeton-methyl (APPENDIX III).

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX II, Attachment II) were followed. The TAL staff prepared application field spikes which occurred around the same time of the ambient test and accurately represented the handling in the field. The field spike results ranged from 109% to 121% for oxydemeton-methyl and 120% to 140% recovery for dioxydemeton-methyl. The complete audit report by the Quality Management and Operations Support Branch (QMOSB) is presented in APPENDIX IV.

Laboratory spikes were prepared by the TAL as well as the ARB's QMOSB. Recovery for the ARB audit spikes averaged 89% and 114% for oxydemeton-methyl and its breakdown product, respectively. The TAL in-house ambient spike recovery levels averaged 99.8% and 122% for these compounds. The complete results of the TAL spikes and QMOSB audit are presented in APPENDIX III and APPENDIX IV, respectively.

TABLE I. Oxydemeton-methyl Ambient Monitoring Sites

Site ID	Address
P	Prunedale School Maintenance Yard 17590 Pesante Road Prunedale, CA 93907
LJ	La Joya School 55 Rogge Road Salinas, CA 93906
C	Chualar School 24285 Lincoln Street Chualar, CA 93925
S	California Department of Forestry Station Route 1 107A Soledad, CA 93960
G	Greenfield Transportation Maintenance Yard 7th Street Extension Greenfield, CA 93927

TABLE II. Oxydemeton-methyl Ambient Monitoring Data

Sample	Time	Volume	Total	Concentration	Collection
ID	(min.)	(m ³)	(ug)	(ug/m ³)	Dates
1P	1390	20.3	ND	--	8/14-15/95
1LJ-1	Lost power				
1LJ-2	Lost power				
1C	1400	20.4	ND	--	
1S	1415	20.7	ND	--	
1G	1415	20.7	ND	--	
1B	BLANK	--	ND	--	8/15-16/95
2P	1420	20.7	ND	--	
2LJ-1	1400	19.0*	ND	--	
2LJ-2	1400	20.4	ND	--	
2C	1410	20.6	ND	--	
2S	1390	20.3	ND	--	
2G	1400	20.4	ND	--	8/16-17/95
3P	1430	20.9	ND	--	
3LJ-1	1430	20.9	ND	--	
3LJ-2	1430	20.9	ND	--	
3C	1420	20.7	ND	--	
3S	1425	20.8	ND	--	
3G	1410	20.6	ND	--	8/17-18/95
4P	1480	21.6	ND	--	
4LJ-1	1440	21.0	ND	--	
4LJ-2	1440	21.0	ND	--	
4C	1385	20.2	ND	--	
4S	1345	19.6	ND	--	
4G	1305	19.1	ND	--	8/21-22/95
5P	1455	19.6*	ND	--	
5LJ	1455	21.2	ND	--	
5C-1	1455	17.8*	ND	--	
5C-2	1455	17.5*	ND	--	
5S	1455	21.2	ND	--	
5G	1460	21.3	ND	--	8/22-23/95
5B	BLANK	--	ND	--	
6P	1425	20.8	ND	--	
6LJ	1425	18.7*	ND	--	
6C-1	1425	20.8	ND	--	
6C-2	1425	15.9*	ND	--	
6S	1435	21.0	ND	--	
6G	1430	19.3*	ND	--	

P = Prunedale, LJ = La Joya School, Salinas, C = Chualar, S = Soledad, G = Greenfield. -1, -2 indicates duplicates taken at the same site.

All flows at 14.6 liters per minute unless noted otherwise.

ND = Not Detected, <0.25 ug/sample (approx. 0.012 ug/m³ for 24 hours).

No values corrected for percentage of recovery.

*Final flow rate different from set value of 14.6 lpm. Volumes corrected.

TABLE II. Oxydemeton-methyl Ambient Monitoring Data (Cont.)

Sample ID	Time (min.)	Volume (m ³)	Total (ug)	Concentration (ug/m ³)	Collection Dates
7P	1465	19.6*	ND	--	8/23-24/95
7LJ	1450	21.2	ND	--	
7C-1	1450	21.2	ND	--	
7C-2	1450	21.2	ND	--	
7S	1400	20.4	ND	--	
7G	1435	21.0	ND	--	
8P	1410	20.6	ND	--	8/24-25/95
8LJ	1385	20.2	ND	--	
8C-1	1320	19.3	ND	--	
8C-2	1320	19.3	ND	--	
8S	1285	18.8	ND	--	
8G	1245	18.2	ND	--	
9P	1500	21.9	ND	--	8/28-29/95
9LJ	1465	21.4	ND	--	
9C-1	1380	20.1	ND	--	
9C-2	1360	19.9	ND	--	
9S	1275	17.6*	ND	--	
9G	1225	15.3*	ND	--	
9B	BLANK	--	ND	--	8/29-30/95
10P	1500	21.9	ND	--	
10LJ	1455	19.7*	ND	--	
10C-1	1435	20.2*	ND	--	
10C-2	1435	17.3*	ND	--	
10S	1465	21.4	ND	--	
10G	1470	21.4	ND	--	8/30-31/95
11LJ	1435	21.0	ND	--	
11C-1	1460	20.0*	ND	--	
11C-2	1465	21.4	ND	--	
11S	1445	17.7*	ND	--	
11G	Lost power				
12P	1500	18.2*	ND	--	8/31-9/1/95
12LJ	1480	17.8*	ND	--	
12C-1	1470	19.5*	ND	--	
12C-2	1460	17.6*	ND	--	
12S	1490	14.7*	ND	--	
12G	1490	18.1*	ND	--	

P = Prunedale, LJ = La Joya School, Salinas, C = Chualar, S = Soledad, G = Greenfield. -1, -2 indicates duplicates taken at the same site.

All flows at 14.6 liters per minute unless noted otherwise.

ND = Not Detected, <0.25 ug/sample (approx. 0.012 ug/m³ for 24 hours).

No values corrected for percentage of recovery.

*Final flow rate different from set value of 14.6 lpm. Volumes corrected.

TABLE II. Oxydemeton-methyl Ambient Monitoring Data (Cont.)

Sample ID	Time (min.)	Volume (m ³)	Total (ug)	Concentration (ug/m ³)	Collection Dates
13P	1375	20.1	ND	--	9/5-6/95
13LJ	1390	20.3	ND	--	
13C	1375	20.1	ND	--	
13S-1	1360	19.9	ND	--	
13S-2	1360	19.9	ND	--	
13G	1365	19.9	ND	--	
13B	BLANK	--	ND	--	
14P	1415	20.7	ND	--	9/6-7/95
14LJ	1405	20.5	ND	--	
14C	1410	20.6	ND	--	
14S-1	1420	20.7	ND	--	
14S-2	1420	20.7	ND	--	
14G	1410	19.7*	ND	--	
15P	1500	21.9	ND	--	9/7-8/95
15LJ	1465	21.4	ND	--	
15C	Lost power				
15S-1	1315	19.2	ND	--	
15S-2	1315	19.2	ND	--	
15G	1265	17.7*	ND	--	

P = Prunedale, LJ = La Joya School, Salinas, C = Chualar, S = Soledad, G = Greenfield. -1, -2 indicates duplicates taken at the same site.

All flows at 14.6 liters per minute unless noted otherwise.

ND = Not Detected, <0.25 ug/sample (approx. 0.012 ug/m³ for 24 hours).

No values corrected for percentage of recovery.

*Final flow rate different from set value of 14.6 lpm. Volumes corrected.

FIGURE I. Oxydemeton Methyl Monitoring Area

